Photoaddition of Acetylenes to Benzene

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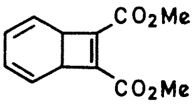
Summary Acetylene photoadds to benzene giving cyclo-octatetraene; the corresponding addition of dimethyl acetylenedicarboxylate occurs *via* intermediate (I), and the addition of methyl phenylpropiolate involves photo-excitation of the acetylene rather than the benzene.

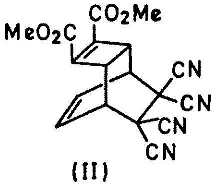
VARIOUS conjugated acetylenes are known to photoadd to benzene, forming the corresponding cyclo-octatetraenes.[1,2] The corresponding addition of acetylene itself has been reported only tentatively, and it was thought possible that the product arose from tetramerisation of acetylene.[2,3] We now report that irradiation (253·7 nm) of acetylene-saturated benzene under nitrogen at 20° gives small amounts (quantum yield estimated to be $< 0{\cdot}001$) of cyclo-octatetraene (identified by g.l.c. and mass spectrometry) as the only C_8 product. Specifically, no trace of semibullvalene was found, so it seems very unlikely that this compound was a precursor of the cyclo-octatetraene. Hexadeuteriobenzene likewise gives 1,2,3,4,5,6-hexadeuteriocyclo-octatetraene; hence, tetramerisation of acetylene is excluded. Similarly, t-butylacetylene and hex-1-yne both form 1 : 1 adducts with benzene, and it has been shown in the latter case at least that the product is n-butylcyclo-octatetraene rather than the 1,3-addition product previously thought possible.[4b]

Very little has been reported on the mechanism of the addition of acetylenes to benzene, and although the possibility of an initial 1,2-cycloaddition was suggested earlier,[1,2] alternatives are readily envisaged. Trapping studies have now shown that the photoaddition of dimethyl acetylene-dicarboxylate to benzene does proceed by way of the bicyclo[3,2,0]octatriene (I) previously suggested[1,2]† Thus, irradiation (253 7 nm) in the presence of tetracyanoethylene at 20° led to formation of a 1 · 1 : 1 adduct (II) (m p 209—211°) at the expense of the cyclo-octatetraene (III) Control experiments established that adduct (II) did not arise by addition of tetracyanoethylene to the cyclo-octatetraene (III) under the conditions employed. This result also excludes the intermediacy of the 1,3-adduct (IV), although mono-olefins[4] are known to photoadd 1,3 to benzene ‡

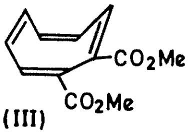
The excited species, previously unidentified, has been shown to be the acetylene rather than the benzene in the case of addition of methyl phenylpropiolate to benzene to form the cyclo-octatetraene (V) In this case the reaction still proceeds readily behind a filter transmitting at wavelengths >290 nm where only the acetylene absorbs to a significant degree Further, solutions of methyl phenylpropiolate in benzene show no appreciable charge-transfer absorption in this region In view of this result, it is specially interesting that an analysis of orbital-symmetry relationships has indicated the possibility of concerted *cis*- or *trans*-1,2-addition of S_1 acetylene to S_0 benzene, but not of S_1 benzene to S_0 acetylene [6]



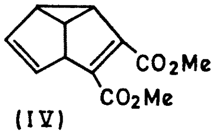
(I)



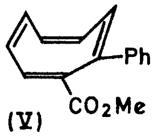
(II)



(III)



(IV)



(V)

(*Received, March 10th, 1970, Com 344*)

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† Later results (D Bryce-Smith, R Deshpande, A Gilbert, and J Grzonka, *Chem Comm*, in the press) suggest strongly that the initial product is not compound (I) but a zwitterion or related species having a significant degree of dipolar character which subsequently transforms into (I)

‡ Liu obtained a mixture of three isomeric semibullvalenes from vapour-phase irradiation of mixtures of hexafluorobut-2-yne and benzene (ref 5) Since the ratio of these products was similar to that obtained by sensitised photoisomerisation of the corresponding thermal 1 4-adduct of the acetylene and benzene the semibullvalenes may not have resulted from direct 1 3-addition to benzene

[1] E Grovenstein and D V Rao *Tetrahedron Letters* 1961 148

[2] D Bryce Smith and J E Lodge *Proc Chem Soc* 1961 333, *J Chem Soc* 1963, 695

[3] Z Kuri and S Shida, *Bull Chem Soc Japan*, 1952, **25**, 116, Z Kuri, *J Chem Soc Japan* 1955, **76**, 944

[4] (a) K E Wilzbach and L Kaplan, *J Amer Chem Soc* 1966, **88**, 2066, (*b*) D Bryce-Smith A Gilbert, and B H Orger *Chem Comm*, 1966 512

[5] R S H Liu and C G Krespan *J Org Chem*, 1969, **34**, 1271

[6] D Bryce-Smith *Chem Comm*, 1969 806